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The synthesis of phosphorylated silsesquioxanes and the investigation of the ability to aggregation and interaction with aromatic dicarboxylic acids

Rushana R. Khairova [a], Luidmila S. Yakimova [a], Vladimir G. Evtugyn [a, c], Ildar Kh. Rizvanov [b], Ivan I. Stoikov [a, d, *]

[a] A. M. Butlerov Chemical Institute, Kazan Federal University, 420008 Kazan, Kremlevskaya 18, Russian Federation
[b] A.E. Arbuzov Institute of Organic and Physical Chemistry of KSC RAS, 420088 Kazan, Acad. Arbuzov 8, Russian Federation
[c] Institute of Fundamental Medicine and Biology, Kazan Federal University, 420008 Kazan, Kremlevskaya 18, Russian Federation
[d] KIBB KazSC RAS, 420111 Kazan, Lobachevsky 2/31, Russian Federation

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ABSTRACT

For the first time, silsesquioxanes containing aminophosphonate fragments were synthesized by condensation of the aminophosphonate derivatives with trialkoxysilane moieties under acid catalysis conditions. According to 29Si NMR, IR-spectroscopies, the silsesquioxane obtained have ladder-like structure with T_4 and T_6 silicon atoms. Information obtained from the MALDI-TOF mass spectra was used to deduce the structure of both oligomeric derivatives and the silsesquioxane framework. The morphology of the polysilsesquioxanes formed was investigated by transmission electron microscopy. The T_6-silsesquioxanes bearing aminophosphonate moieties contrary to T_4-silsesquioxanes tend to form aggregates of prolate shape. Their aggregation behavior was analyzed by the dynamic light scattering method. T_6-silsesquioxane tends to form submicron-sized aggregates in aqueous solutions. The ability of these silsesquioxanes to recognize aromatic dicarboxylic acids was studied by the UV-spectroscopy.

Introduction

The synthesis of macromolecules and materials able to molecular recognition of various substrates is one of the main recent research tendencies. For realization of the ability to bind and recognize molecules, polyfunctional moieties containing both acceptor and donor groups are usually introduced in the synthetic receptor structure. Thus, aminophosphonate derivatives provide significant interest due to presence of proton acceptor (phosphoryl and) proton donor (amino groups) [1], from which the acid is an analog of natural compounds used in medicine [2]. It was shown that aminophosphonates exert high antiviral [3], antibacterial [4], antifungal [5], antimicrobial [6], and antitumor activity [7].

Meanwhile the development of low-cost materials becomes relevant. The silicon derivatives are excellent from this point of view. Concerning silsesquioxanes with empirical formulas $SiO_{3/2}$, it should be noted that even though silsesquioxane chemistry spans over a half of the century, the interest continues to increase [8]. Synthesis of silsesquioxanes with the specified structure has been studied previously [9–13]. Nevertheless the study of the conditions for polycondensation of the organosilicon derivatives and their products calls for more careful investigation. Due to the low toxicity and high thermomechanical stability the appropriate materials based on silsesquioxanes are quite competitive and demanded.

Therefore, we have proposed the hypothesis that the combination of silsesquioxane as a core of hybrid materials containing simultaneously proton donor and acceptor groups can lead to selective receptor function toward biological substrates. Nano-sized building blocks and their capability to effectively recognition of biologically relevant substrates [14,15], combined with low toxicity and availability make it promising to study the condensation products of the organosilicon derivatives.

Thus, the synthesis silsesquioxanes containing aminophosphonate fragments by polycondensation of the aminophosphonate derivatives with trialkoxysilane moieties under acid catalysis conditions and investigating their ability to recognize aromatic dicarboxylic acids is the main goal of this work.

* Corresponding author. A. M. Butlerov Chemical Institute, Kazan Federal University, 420008 Kazan, Kremlevskaya 18, Russian Federation.
E-mail address: ivan.stoikov@mail.ru (I.I. Stoikov).

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